De conformatie van enige ortho-tertiairbutylverbindingen en van de dithienyllen

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SUMMARY

THE STRUCTURE OF 4,5-DI-T-BUTYLIMIDAZOLE AND 2,3-DI-T-BUTYLQUINOXALINE

The synthesis of *o*-di-*t*-butyl heteroaromatics has involved difficulties, because of steric hindrance between the *t*-butyl groups. To obtain more information about the strain in these molecules, the structures of two *o*-di-*t*-butyl heteroaromatics, viz. 4,5-di-*t*-butylimidazole (DTBI) and 2,3-di-*t*-butylquinoxaline (DTBC), have been determined by X-ray diffraction. Both compounds are monoclinic, space groups $P2_1/n$ and $P2_1/c$ respectively, with two independent molecules per cell. The experimental part of the structure determinations is described in chapter 2 (DTBI) and chapter 3 (DTBC). The intensities of the reflexions of DTBC were measured on an automated Nonius diffractometer at room temperature and at low temperature (-155°C), those of DTBI were collected at low temperature only. The structure models were found by means of the symbolic addition method (Karle and Karle, 1966), using the low temperature (L.T.) intensities of DTBI and the room temperature (R.T.) intensities of DTBC. The coordinates and anisotropic thermal parameters of the 'heavy' atoms were refined by least-squares techniques. Hydrogen atoms were introduced with isotropic temperature factors, with fixed parameters for DTBI and variable parameters for DTBC. The indices R at the end of the refinements are 0.085 (DTBI; 5359 reflexions), 0.072 (DTBC, R.T.; 3296 refl.) and 0.062 (DTBC, L.T.; 8324 refl.). The estimated standard deviations in bond lengths and angles are 0.005 Å and 0.35° for DTBI, 0.005-0.007 Å and 0.4° for DTBC (R.T.) and 0.0035 Å and 0.23° for DTBC (L.T.).

The results are discussed in chapter 4. The two crystallographic non-equivalent molecules of DTBC show an interesting difference. In one of the molecules the quinoxaline group is approximately planar, whereas in the other one this group has a somewhat twisted structure. The non-

planar quinoxaline group lies at shorter distances from its neighbours in the crystal than the planar one. Therefore the deviations from planarity have probably to be ascribed to intermolecular interaction in the crystal; they are not due to steric hindrance of the *t*-butyl substituents. A similar phenomenon, although less pronounced, occurs in DTBI. Apart from the differences in conformation mentioned above no essential differences have been observed between the corresponding independent molecules at low temperature, and between the room and low temperature structure of DTBC. In the crystal structure of DTBI the molecules have formed chains in which they are linked by N-H...N hydrogen bonds of 2.04 and 1.98 Å.

The conformation of the *t*-butyl groups is discussed in chapter 5. In DTBC, DTBI and in 1,2,4,5-tetra-*t*-butylbenzene (TTBB) investigated by v. Bruijnsvoort, Eilermann, v.d. Meer and Stam (1968) essentially the same conformation has been observed for the *o*-*t*-butyl groups. In each of the molecules the *o*-*t*-butyl groups are related by pseudo twofold symmetry and fit together like gear wheels (Fig. 5.1c and d). The angles around the quarternary carbon atoms are deformed such as to release the strain between the groups. Between the *t*-butyl groups in DTBC there are six C...C distances shorter than 3.50 Å, the remaining distances are larger than 3.90 Å. For DTBI these distances are 3.67 and 4.00 Å respectively, and for TTBB 3.46 and 3.90 Å.

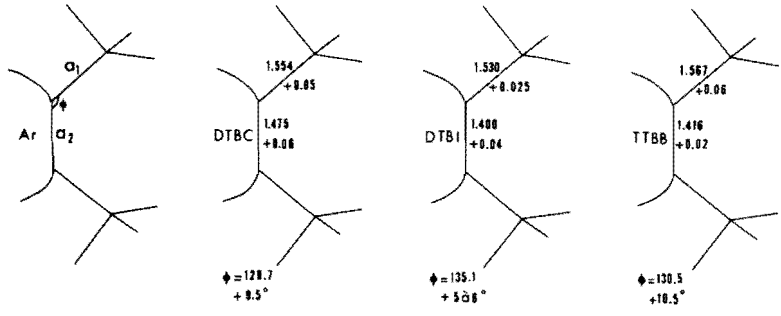

Fig. S1 The values of a_1, a_2 and φ with their deformations. Ar = aromatic compound.

The angles φ and the bonds a_1 and a_2 (see Fig. S1) are affected most by the presence of the *t*-butyl groups. The

values estimated for the deformations are given in the figure. It appeared to be difficult to get accurate estimates for the deformations, as not in all cases reliable values for corresponding bonds in unstrained compounds, e.g. with CH_3 in stead of *t*-butyl, were available. The difference in Δa_2 obtained for TTBB and DTBC has not been explained yet. Except for Δa_2 (DTBC) and Δa_2 (DTBI) all Δ-values can be correlated with force constants from the literature via a simple model given for the strain energy in *o*-*t*-butyl heteroaromatics by Wiebenga and Bouwhuis (1969). In this model the strain energy in the molecule is considered as a function of the distance between the quarternary carbon atoms of the *t*-butyl groups and the deformations of a_1, a_2 and φ.

THE DITHIENYLS

The crystal structures of the three isomeric dithienyls $C_8H_6S_2$ have been determined by X-ray diffraction. The main purpose of this study was to check whether or not the molecules in the solid state would be planar as is the case for biphenyl (Trotter, 1961). Many difficulties were encountered during the structure determinations. It appeared to be difficult to grow good crystals of the compounds, the crystals of 2,2'-dithienyl decomposed during X-ray exposure and those of 2,3'- and 3,3'-dithienyl (and possibly also those of 2,2'-dithienyl) appeared to show disorder. None of the structures could therefore be determined with great accuracy. Nevertheless it could be concluded that all three dithienyls are planar in the solid state.

The bond lengths in the thienyl groups do not differ significantly from those in thiophene. For 2,2'- and 3,3'-dithienyl it is certain that the majority of the molecules in the crystals has the, centrosymmetric, *anti* conformation although it cannot be excluded that a minority (less than 30%) is in the *syn* form. Disorder as observed in 3,3'-dithienyl appeared also to be present in thiophene-3-carboxylic acid (Hudson and Robertson, 1964). For 2,3'-dithienyl disorder is complete and no information is available about the conformation in the plane of the molecule.

The packing of the molecules in the crystals is similar

for the three dithienyls. In all cases the planes of the molecules make an angle of approximately 30° with a short crystal axis of approximately 5.5 Å. Theoretical calculations as done for biphenyl by Casalone, Mariani, Mugnoli and Simonetta (1968) to understand the difference in conformation between the molecules in the gaseous and in the solid phase, have not been attempted for the dithienyl molecules.